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# Processing Irradiated Beryllium for Disposal

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Troy J. Tranter
Richard D. Tillotson
Nick R. Mann
Glen R. Longhurst

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# PROCESSING IRRADIATED BERYLLIUM FOR DISPOSAL

TROY J. TRANTER*, RICHARD D. TILLOTSON, NICK R. MANN, GLEN R. LONGHURST *Idaho National Laboratory, P.O. Box 1625, Idaho Falls, Idaho, 83415 USA*

## ABSTRACT

*The purpose of this research was to develop a process for decontaminating irradiated beryllium that will allow it to be disposed of through normal rad-waste channels. Thus, the primary objectives of this ongoing study are to remove the transuranic (TRU) isotopes to less than 100 nCi/g and remove $^{60}Co$, and $^{137}Cs$, to levels that will allow the beryllium to be contact handled. One possible approach that appears to have the most promise is aqueous dissolution and separation of the isotopes by selected solvent extraction followed by precipitation, resulting in a granular form for the beryllium that may be fixed to prevent it from becoming respirable and therefore hazardous. Beryllium metal was dissolved in nitric and fluorboric acids. Iosotopes of $^{241}Am$, $^{239}Pu$, $^{85}Sr$, and $^{137}Cs$ were then added to make a surrogate beryllium waste solution. A series of batch contacts was performed with the spiked simulant using chlorinated cobalt dicarbollide (CCD) and polyethylene glycol diluted with sulfone to extract the isotopes of Cs and Sr. Another series of batch contacts was performed using a combination of octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in tributyl phosphate (TBP) diluted with dodecane for extracting the isotopes of Pu and Am. The results indicate that greater than 99.9% removal can be achieved for each isotope with only three contact stages.*

**KEYWORDS:** *beryllium, disposition, transuranic, $^{137}Cs$*

## I. INTRODUCTION

Beryllium is used in numerous research reactors throughout the world to moderate neutron energies and reflect neutrons back into the core, thus intensifying the thermal neutron flux. Beryllium is also being considered for plasma-facing surfaces in future fusion reactors. However, beryllium has a finite life span in a reactor because of the particle reactions (n,2n & n,$\alpha$), which result in the production of $^{4}He$, $^{3}He$, and $^{3}H$. Over time, the accumulation of helium and hydrogen atoms causes the beryllium to swell, requiring it to be replaced periodically. There are also various impurities or "tramp" materials in the beryllium that undergo neutron capture reactions and produce radionuclides. Recent investigations of impurities in the beryllium such as nitrogen and uranium, indicate they undergo nuclear reactions to generate isotopes such as $^{14}C$, $^{137}Cs$, $^{60}Co$, and several transuranic (TRU) isotopes. Thus in addition to the issues surrounding health hazards associated with beryllium, the presence of these radioisotopes makes it a very problematic material with respect to waste disposal. To date, a permanent disposal pathway for highly irradiated beryllium has not been identified.

With respect to the Idaho National Laboratory (INL), used beryllium reflector material (Fig. 1) currently occupies canal space that is needed for other activities and plans for continued Advanced Test Reactor (ATR) operation dictate that this material must eventually be disposed of or otherwise transferred to another temporary storage.

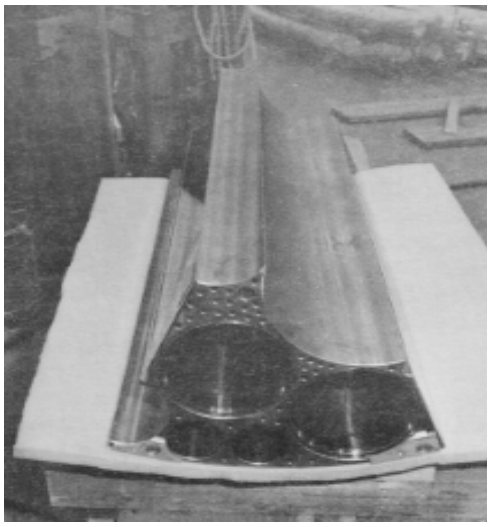

Fig. 1. This ATR reflector block, like beryllium from many reactors, requires decontamination for disposal.

Several studies over the last few years have demonstrated that beryllium irradiated in INL reactors

*E-mail: Troy.Tranter@INL.gov

exceeds the criterion for classification as transuranic (TRU) waste, and most of it is greater than Class-C as specified in 10 CFR 61 [1,2]. This situation raises concerns for disposal of irradiated beryllium components now in the ATR canal and in the Engineering Test Reactor (ETR). It also impacts the approvals required to proceed with core internals change-outs at ATR.

A recent study of beryllium irradiated in the ETR has shown the isotopes in Table 1 to be of concern in that beryllium Estimates for radionuclide concentrations in ATR beryllium are similar to the values listed in Table 1.

Table 1. Isotopes of concern in beryllium irradiated in the ETR.

| Isotope | Activity (Ci) | TRU Fraction | Class C Fraction |
|---|---|---|---|
| H-3 | 79,880.000 | | |
| C-14 | 7.237 | | 0.2319 |
| Nb-94 | 0.020 | | 0.2565 |
| Pu-238 | 0.212 | 2.9431 | 2.9431 |
| Pu-239 | 0.030 | 0.4193 | 0.4193 |
| Pu240 | 0.044 | 0.6047 | 0.6047 |
| Pu-241 | 3.893 | | 53.9428 |
| Am-241 | 0.388 | 5.3790 | 5.3790 |
| Cm-244 | 0.753 | | 10.4283 |

To date, some research has been done regarding the conditioning of irradiated beryllium waste into leach resistant forms [3]. But, a preliminary search of the literature indicates that little work has been performed to develop a viable separation and treatment alternative for this waste stream. To eliminate concerns for disposal, TRU contributors, particularly Pu and Am, need to be removed. We have determined that if 99% of these metals were removed, these disposal issues would be resolved.

The objective of the work presented herein was to develop a process for decontaminating irradiated beryllium that will allow it to be disposed of through normal rad-waste channels. Thus, the primary objectives were to remove the TRU isotopes to levels below 100 nCi/g and remove isotopes of cesium and strontium to levels that will allow the beryllium to be contact handled. One possible approach that appears to have promise is aqueous dissolution and separation of the isotopes by selected solvent extraction followed by precipitation or other treatment [3], resulting in a granular form for the beryllium that may be fixed to prevent it from becoming respirable and therefore hazardous.

## II. BERYLLIUM DISSOLUTION

The INL research team has extensive experience with myriad separation schemes for quantitatively separating the TRU and fission product isotopes of interest [4-9]. However, many of the preferred techniques utilize solvent extraction approaches where nitric acid is necessary to form the neutral acid adduct. Thus in order to be compatible with the proposed separation flow sheets, it was necessary to develop a technique for dissolving beryllium metal in nitric acid. To overcome the passivation effect of nitric acid on the metal, i.e. the formation of beryllium oxide, fluoroboric acid was used as a catalyst according to the following reactions:

$$3H_2O + HBF_4 \rightarrow 4HF + H_3BO_3$$
$$HNO_3 + Be \rightarrow BeO + H^+ + NO_2^-$$
$$4HF + 2BeO \rightarrow 2BeF_2 + 2H_2O$$
$$2BeF_2 + 4H^+ + 4NO_3^- \rightarrow 2Be(NO_3)_2 + 4HF \quad (1)$$

Approximately 8 grams of unirradiated beryllium metal were dissolved in 250 milliliters of nitric acid at 90ºC according to the reactions in (1), which resulted in a final solution of approximately 32 grams of beryllium per liter. When cooled the solution remained clear and visible solids were not present. Aliquots of this beryllium feed solution were removed and spiked with tracers of $^{137}$Cs, $^{85}$Sr, $^{241}$Am, and $^{239}$Pu to simulate the contamination from these isotopes in actual irradiated beryllium reflector material. The acidity of some of the aliquots was also adjusted by dilution with de-ionized water to yield solutions of three different acid concentrations between approximately 1.5 and 6 molar. Aliquots of these acid adjusted solutions were removed and analyzed via inductivley coupled plasma mass spectro-metry (ICPMS) to determine total beryllium concentration. These aliquots were also analyzed via gamma spectrometry to measure the total concentrations of $^{137}$Cs, $^{85}$Sr, and $^{241}$Am. The $^{239}$Pu concentration was measured by liquid scintillation counting (LSC).

## II. SEPARATIONS

It was postulated that chlorinated cobalt dicarbollide (CCD) and polyethylene glycol diluted with sulfone would be effective for extracting the Cs and Sr isotopes from the dissolved Be solution, and that a combination of octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in tributyl phosphate (TBP) diluted with dodecane would be efficacious for removing the Am and Pu isotopes. Thus, a series of batch contacts was

performed with the spiked beryllium solutions and the selected solvents to determine the solvent extraction efficiency for the various elements. To accomplish this an aliquot of the organic solvent was contacted three times, each with fresh aliquots of the aqueous Be feed solution at an organic:aqueous ratio equal to 1.0 as depicted in Fig. 2.

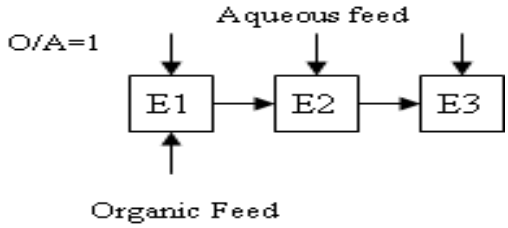


Fig. 2. Contacting sequence for solvent extraction batch experiments.

The contacts were achieved by placing the organic – aqueous mixtures in 25 milliliter glass test tubes, mixing for one minute on a vortex mixer, followed by centrifugation. After the phases were separated, aliquots of the aqueous and organic fractions were quantitatively removed for analysis. The activities of $^{137}$Cs, $^{85}$Sr, and $^{241}$Am were determined by gamma spectrometry and $^{239}$Pu was measured by LSC.

Fig. 3. Solvent extraction batch contact.

## IV. RESULTS

As a measure of the capability of the organic solvent to extract the target isotopes, a distribution coefficient ($D$) was calculated for each of the batch contacts according to the following equation:

$$D = \frac{\textit{isotope concentration in organic phase (Bq/ml)}}{\textit{isotope concentration in aqueous phase (Bq/ml)}} \quad (2)$$

The results of the batch experiments are given for the $^{137}$Cs-$^{85}$Sr-CCD system in Table 2. The results of the batch tests for the $^{241}$Am-$^{239}$Pu-CMPO-TBP system are presented in Table 3. In the sample column of each of the tables, the numbers 5.8, 2.9, and 1.5 specify the nitric acid molarity and the E1 – E3 labels refer to the contact number as shown in Fig. 1 above.

It can be seen from the results listed in Tables 2 and 3 that the distribution coefficients for each of the isotopes were much greater than one in all cases. The results indicate that greater than 99.9% removal can be achieved for each isotope with only three contact stages. Increasing the number of extraction stages should provide even greater removal efficiencies. It should be noted that data are not presented for the 5.8 molar nitric acid fraction for Am and Pu. This is due to the fact that third phase formation was seen at this acid concentration. The best removal was seen for $^{137}$Cs at a nitric acid concentration of 1.5 molar, while the highest distribution coefficients were achieved for the other isotopes at a nitric acid concentration of 2.9 molar. However, the $D_{Cs\text{-}137}$ values were still approximately 80 at the 2.9 molar nitric acid concentration. Thus, the overall separation process should function quite well at a nitric acid concentration between 2 and 3 molar. The mass balance, which is the sum of the total isotope amount recovered in the aqueous and organic phases divided by the total amount initially present in the feed, was between 95 and 110% for all contacts.

Table 2. Distribution coefficient results for $^{137}$Cs and $^{85}$Sr.

| Sample | $D_{Cs\text{-}137}$ | Mass Bal (%) | $D_{Sr\text{-}90}$ | Mass Bal (%) |
|---|---|---|---|---|
| 5.8 E1 | 2.59E+01 | 103.1 | 1.67E+02 | 103.5 |
| 5.8 E2 | 2.41E+01 | 97.3 | 1.77E+02 | 97.4 |
| 5.8 E3 | 2.07E+01 | 101.3 | 1.49E+02 | 101.4 |
| 2.9 E1 | 8.71E+01 | 102.2 | 8.62E+02 | 102.5 |
| 2.9 E2 | 7.99E+01 | 102.2 | 8.70E+02 | 102.2 |
| 2.9 E3 | 6.66E+01 | 97.1 | 7.05E+02 | 97.4 |
| 1.5 E1 | 1.66E+02 | 102.8 | 1.06E+02 | 102.5 |
| 1.5 E2 | 1.66E+02 | 100.0 | 1.89E+02 | 100.2 |
| 1.5 E3 | 1.48E+02 | 102.2 | 1.87E+02 | 102.4 |

It should be noted that the organic fractions were also analyzed for beryllium and that statistically significant quantities were not present in this phase. As expected, this indicates that the beryllium did not extract into either of the organic solvent systems used for separating the radionuclides and that an acid scrub could be used to ensure that any physically entrained beryllium is adequately washed from the organic

Table 3. Distribution coefficient results for $^{241}$Am and $^{239}$Pu.

| Sample | $D_{Am-241}$ | Mass Bal (%) | $D_{Pu-239}$ | Mass Bal (%) |
|---|---|---|---|---|
| 2.9 E1 | 5.07E+02 | 107.9 | 1.83E+02 | 102.5 |
| 2.9 E2 | 7.40E+02 | 102.6 | 3.94E+02 | 102.2 |
| 2.9 E3 | 6.67E+02 | 101.3 | 3.01E+01 | 97.4 |
| 1.5 E1 | 1.52E+02 | 104.4 | 1.12E+01 | 102.5 |
| 1.5 E2 | 1.80E+02 | 101.1 | 1.60E+01 | 100.2 |
| 1.5 E3 | 1.37E+02 | 100.7 | 9.13E+00 | 102.4 |

phase. Since beryllium was not extracted, it is not the source of the third phase formation seen at the highest acid concentration in the TBP-CMPO system. Third phase formation is typically the result of a metal extracting in high concentrations into the organic phase. A high concentration of the organic-metal complex causes the organic phase to physically partition into an organic rich and deficient phase. Thus, it is suspected that a metal impurity in the beryllium used for the feed solution may be the cause of the single case of third phase formation. This hypothesis is currently being investigated.

## V. CONCLUSIONS

The work performed during this research effort has shown that beryllium can be successfully dissolved in nitric acid and that isotopes of Cs, Sr, Pu, and Am can be successfully removed using a combination of two solvent extraction approaches. The data suggest that three extraction stages utilizing a contacting regime with high efficiency, e.g. centrifugal contactors, would result in greater than 99.9% removal of the radionuclides.

Work will continue to develop a suitable technique for $^{60}$Co removal. Column supported dimethyl glyoxime will be investigated for this purpose as well as several ion exchange approaches. Work will also continue with the target isotopes mentioned above to investigate the possibility of using a combination of extraction chromatography and ion exchange to provide an alternative approach to solvent extraction for removing these isotopes.

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